WET ETCHING APPARATUS AND WET ETCHING METHOD USING ULTRAVIOLET LIGHT

1. Field of the Invention

The present invention relates to a semiconductor manufacturing apparatus, and specifically to a wet etching apparatus and a wet etching method.

2. Description of the Background Art

In recent years, a high-dielectric-constant film (hereafter referred to as "high-k dielectric film") is used as a gate insulating film for an advanced device. The high-k dielectric film is acceleratedly densified by heat treatment (i.e. annealing) performed after film formation, and high-k dielectric film is changed to have properties difficult to etch.

Heretofore, for etching of films to be etched, there have been used wet etching wherein a film to be etched is made to contact a chemical solution and etching is performed by an etchant dissociated in the chemical solution; and dry etching wherein radicals and ionic species excited in plasma are drawn in a substrate to forcedly etching a film to be etched.

However, there has been the problem of very low etching rate when a dense thin film, such as a high-k dielectric film after annealing, is subjected to wet etching. Therefore, there has been the problem of significantly low throughputs.

When a dense thin film is subjected to dry etching in place of wet etching, there has been a problem that although a higher etching rate is obtained than wet etching, the base member that should not be etched is continuously etched. That is to say, there has been a problem that a sufficient etching selectivity to the base member cannot be obtained by dry etching.

Heretofore, such difficulty of etching has been a drawback when a high-k dielectric film is applied to advanced devices.

SUMMARY OF THE INVENTION

The present invention has been conceived to solve the previously-mentioned problems and a general object of the present invention is to provide a novel and useful wet etching apparatus and is to provide a novel and useful wet etching method.

A more specific object of the present invention is to provide a wet etching apparatus and a wet etching method having a high etching selectivity to a base member below a film to be processed, and having a high etching rate.

The above object of the present invention is attained by a following wet etching apparatus and a following method for wet etching of a film.

According to one aspect of the present invention, the wet etching apparatus comprises a chemical-solution supply component for supplying a chemical solution on a film to be processed on a substrate. An ultraviolet-light radiating component radiates ultraviolet light to the film through the chemical solution.

According to another aspect of the present invention, in the method for wet etching of a film, a chemical solution is supplied on a film to be processed on a substrate. Ultraviolet light is radiated to the film through the chemical solution.

Other objects and further features of the present invention will be apparent from the following detailed description when read in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic sectional view for illustrating a wet etching apparatus according to a first embodiment of the present invention;

Fig. 2 is a schematic sectional view for illustrating a wet etching apparatus according to a second embodiment of the present invention;

Fig. 3 is a top view showing vicinity of a substrate in the wet etching apparatus shown in Fig. 2; and

Fig. 4 is a sectional view for illustrating a substrate to be wet etched.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following, principles and embodiments of the present invention will be described with reference to the accompanying drawings. The members and steps that are common to some of the drawings are given the same reference numerals and redundant descriptions therefore may be omitted.

First Embodiment

Fig. 1 is a schematic sectional view for illustrating an etching apparatus according to a first embodiment of the present invention. Specifically, Fig. 1 is a diagram for illustrating an etching apparatus for wet etching of a film to be etched formed on a substrate.

As Fig. 1 shows, a substrate 11 to be wet etched is rotatably held on a rotating stage 5. Specifically, a plurality of pins 4 are installed on the rotating stage 5, and the end portion (edge portion) of the substrate 11 is held between these pins 4. The substrate 11 may also be held using an electrostatic chuck.

A rotating shaft 6 is disposed on the center of the rotating stage 5, and when the rotating stage 5 rotates around the rotating shaft 6, the substrate 11 is also rotates at a desired rotating speed. The rotating stage 5 rotates at a rotating speed of, for example, about 300 to 500 rpm during coating of a chemical solution, and about 2,000 to 3,000 rpm during drying.

As Fig. 4 shows, a film to be etched (film to be processed) 11a is formed on the substrate 11 serving as a base member, and a mask 11b is formed on the film 11a. The film 11a is, for example, a dense

thin film such as a high-k dielectric film. The high-k dielectric film is, for example, HfO_2 film and HfAlO film formed using an ALD (atomic layer deposition) method and performed an annealing (PDA: post deposition annealing) treatment after film formation.

A chemical solution 9 is supplied to the surface of the film to be etched on the substrate 11 through a nozzle 8 installed on the end of a chemical pipe 7. The chemical-solution pipe 7 is connected to a chemical tank (not shown) for storing the chemical solution, or to a chemical-supply line of an incidental apparatus (not shown)through a valve 7a and a pump 7b.

A chemical solution 9 containing, for example, a phosphoric-acid-based etchant may also be used. In order to obtain desired properties, a surface active agent or the like may be added to the chemical solution 9.

Lamp house 2 stores a lamp 1. Lamp house 2 accommodating a lamp 1, which radiates ultraviolet light to the film (11a) through the chemical solution 9, is disposed above the substrate 11. The lamp 1 serving as a light source is, for example, KrCl (wavelength: 222 nm), Xe_2 (172 nm), Kr_2 (147 nm), Ar_2 (126 nm) excimer lamps or the like. Here, the lamp 1 radiates ultraviolet light at energy higher than binding energy of constituent molecules of the film to be etched (11a). Energy of the ultraviolet light can be controlled by a radiating time of the ultraviolet light. The radiating time is, for example, 10 to 200 sec.

The materials of the chemical solution 9 and the thickness of the film to be etched (11a) are selected so as to attain a high transmissivity for the wavelength of the ultraviolet light radiated from the lamp 1.

On the lower surface of the lamp house 2 is formed an opening having the size same as, or larger than the size the substrate 11. This opening is covered with a light-transmitting window 3 formed by a material that transmits ultraviolet light from the lamp 1. The

light-transmitting window 3 is, for example, a window formed of quartz glass (hereafter referred to as "quartz glass window").

The inside of the lamp house 2 sealed with the quartz glass window 3 is filled with an inert gas such as nitrogen. Thereby, a lamp 1 having a wavelength absorbed in the presence of oxygen can be used. Illuminance of the ultraviolet light at the quartz glass window 3 is preferably 5 to 20 mW/cm^2.

On the upper surface of the lamp house 2 is installed a drive unit 10 for driving the lamp house 2 in the vertical direction. The drive unit 10 drives the lamp house 2 to vicinity of the substrate 11 when ultraviolet light is radiated, thereby acting the ultraviolet light from the lamp 1 to the film (11a) in the close distance. Specifically, the lamp house 2 is disposed so that the quartz glass window 3 is disposed 2 to 5 mm above the surface of the substrate 11.

Next, the operation of the etching apparatus, that is the wet etching of the film to be etched will be described.

First, the substrate 11, which has an HfO_2 film serving as the film to be etched (11a) and the mask (11b), is held by pins 4 on the rotating stage 5. The chemical solution 9 containing a phosphoric-acid-based is supplied on the substrate 11 from the nozzle 8, while rotating the substrate 11 at a rotation speed of 300 to 500 rpm by rotating the rotating stage 5 around the rotating shaft 6. Thereafter, when the chemical solution 9 is sufficiently thinly and evenly spread on the substrate 11, the rotation of the substrate 11 is stopped. At this time, the chemical solution 9 has been applied on the entire surface of the substrate 11 in a desired thickness without running off the substrate 11.

The lamp house 2 is lowered by the drive unit 10 so that the quartz glass window 3 locates 2 to 5 mm above the surface of the substrate 11 without interfering the pins 4. Ultraviolet light is radiated from the lamp 1 that has previously been turned on to the HfO_2 film

through the chemical solution 9. At this time, energy of the ultraviolet light breaks the Hf-O bonds of the HfO_2 film, and etching reaction proceeds by etchant contained in the chemical solution 9 previously applied on the substrate 11.

After desired etching has been completed, radiating of the ultraviolet light from the lamp 1 is stopped, the lamp house 2 is elevated with by the drive unit 10. Ultra-pure water is supplied from the water-cleaning nozzle (not shown) on the substrate 11 to wash away the chemical solution 9 remaining on the substrate 11.

Thereafter, the substrate 11 is rotated at about 2,000 to 3,000 rpm with the rotating stage 5 to sprinkle the ultra-pure water and to dry the substrate 11.

In the first embodiment, as described above, after a chemical solution 9 has been applied to dense film to be etched, ultraviolet light having energy larger than binding energy of constituent molecules of the film to be etched is radiated to the film to be etched through the chemical solution 9. Since the ultraviolet light breaks the bonds of the molecules of the film to be etched, the etching rate of the film to be etched contacting the chemical solution 9 is significantly increased. In other words, by wet etching performed in the state wherein the most molecular bonds of the film to be etched have been broken, the etching rate can be significantly increased. Therefore, the time of etching process can be shortened, and the throughput can be improved. Also because of a high etching selectivity to the base member (i.e. substrate 11), the problem of continuous etching of the base member, as in the use of dry etching, does not arise. Thereby, a dense high-k dielectric film can be used in advanced semiconductor devices.

The chemical solution 9 used in the first embodiment has a high transmissivity to the wavelength of the lamp 1. Therefore, little ultraviolet light radiated from the lamp 1 is absorbed by the chemical solution 9, and the ultraviolet light having sufficient light energy

can reach the film to be etched. Thus, the loss of light energy of ultraviolet light by the chemical solution 9 can be decreased as much as possible.

The etching rate can further be improved by elevating the temperature of the chemical solution 9 and/or the substrate 11 using a heat exchanger or a hot plate. In this case, however, the quantity of vaporized chemical solution 9 increases, and cloud of the surface of the quartz glass window 3 on the bottom of the lamp house 2 may occur due to condensation of the vapor. The haze may scatter the ultraviolet radiation, thereby causing insufficiency of the action of the ultraviolet radiation to the film to be etched.

To cope with this problem, it is preferable to apply a surface-active agent having hydrophobic groups, or the like, to the quartz glass window 3. The film of the surface-active agent prevents the condensation of the vaporized chemical solution 9 on the quartz glass window 3, and can prevent the loss of the light energy of ultraviolet light (the same applies to the second embodiment described below).

It is also considered that the quantity of the etchant in the chemical solution 9 is insufficient by a single application of the chemical solution 9, and the etching reaction ceases in the middle. In the case where the supply of the etchant becomes the rate-limiting factor, it is recommended the lamp house 2 is once separated (elevated) from the vicinity of the substrate 11 using the drive unit 10 to supply the chemical solution 9 again from the nozzle 8, and the lamp house 2 is again lowered to the vicinity of the substrate 11 to radiate ultraviolet light again.

However, when the supply of the etchant significantly becomes the rate-limiting factor due to the mechanism of the etching, since the supply of the chemical solution and the radiation of the ultraviolet light must be repeated many times, the processing time increases, and the throughput lowers. There also is a case where the chemical

solution 9 dries up due to heat given by the light energy of ultraviolet light radiated after the application of the chemical solution 9, and an irreversible state may occur during water cleaning after wet etching. The effective means in such a case will be described below as a second embodiment.

In the first embodiment, the case where the film to be etched was a high-k dielectric film was described. However, the present invention is not limited thereto, but can be applied to a film having a low wet-etching rate, and is particularly preferable to a dense thin film (the same applies to the second embodiment described below).

As a comparative example of the first embodiment, the present inventors first radiated ultraviolet light from the lamp 1 to the film to be etched, and then the chemical solution 9 was applied on the film to be etched. However, in the comparative example, increase in the etching rate was little compared with the first embodiment, and the desired effect could not be achieved.

Second Embodiment

Fig. 2 is a schematic sectional view for illustrating an etching apparatus according to a second embodiment of the present invention; and Fig. 3 is a top view showing vicinity of a substrate in the etching apparatus shown in Fig. 2.

The etching apparatus according to the second embodiment is particularly suitable in the case where supply of an etchant significantly becomes the rate-limiting factor as described above.

As Fig. 2 shows, a substrate 11 to be etched is held on a plate-like stage 12 having a wider area than the substrate 11. On the stage 12 are installed a plurality of pins 4 having a height of, for example, 2 to 5 mm, and the end portion (edge portion) of the substrate 11 is held between these pins 4. As Fig. 4 shows, a film to be etched (film to be processed) 11a is formed on the substrate 11, and a mask 11b is formed on the film 11a. The film 11a is, for example, a dense thin film such as a high-k dielectric film. The high-k dielectric

film is, for example, HfO_2 film and HfAlO film formed using an ALD (atomic layer deposition) method, and annealing (PDA: post deposition annealing) treatment.

As in the first embodiment, the lamp house 2 accommodating a lamp 1 is driven by the drive unit 10 in the vertical direction. When ultraviolet light is radiated, the lamp house 2 is disposed so that the quartz glass window 3 is disposed 2 to 5 mm above the surface of the substrate 11.

In the gap between the quartz glass window 3 and the substrate 11, a tip portion 13a of a slit-like flat nozzle 13 is inserted. Chemical solution 9 is continuously supplied to the gap from the flat nozzle 13. Here, as Fig. 3 shows, on the stage 12, a pair of guides 16 are formed so as to be parallel to the flat nozzle 13 and so as to sandwich the substrate 11. Thereby, the chemical solution 9, supplied to an end of the substrate 11 from the flat nozzle 13, is guided by the guides 16 in the direction of the other end of the substrate 11 facing the end (i.e., the direction opposite from the flat nozzle 13), and gradually fills the gap. Furthermore, the excess of the chemical solution 9 supplied from the flat nozzle 13 runs out in the direction opposite from the flat nozzle 13.

The flat nozzle 13 is connected to an end of a pipe 15. The other end of the pipe 15 is connected, through a switching valve 14, to a pipe 15a for chemical solution and a pipe 15b for ultra-pure water. Specifically, the switching operation of the switching valve 14 connects the flat nozzle 13 to the pipe 15a or the pipe 15b through the pipe 15. That is to say, the flat nozzle 13 is connected to a chemical-solution supply line or a ultra-pure-water supply line by switching the switching valve 14.

Next, the operation of the above-descried etching apparatus, that is the wet etching of the film to be etched will be described.

First, a substrate 11, which has an HfO_2 film serving as the film to be etched (11a) and mask (11b), is held by pins 4 on the stage 12.

Then, the lamp house 2 is lowered with the drive unit 10 so that the quartz glass window 3 locates 2 to 5 mm apart from the surface of the substrate 11 without interfering the pins 4.

Next, the tip portion of the flat nozzle 13 is inserted in the gap between the quartz glass window 3 and the substrate 11 from the side to continuously supply the chemical solution 9 from the flat nozzle 13 into the gap. At the same time as the supply of the chemical solution 9, ultraviolet radiation is radiated from the lamp 1 onto the HfO_2 film through the chemical solution 9.

At this time, the light energy of the ultraviolet radiation breaks the Hf-O bonds of the HfO_2 film, and the etchant contained in the chemical solution 9 supplied from the flat nozzle 13 proceeds the etching reaction. The chemical solution 9 supplied from the flat nozzle 13 is led by the guide 16 to the opposite side of the flat nozzle 13, and gradually enters into the gap, and finally fills the gap. By further continuing the supply of the chemical solution 9 at a constant flow rate, the excessive chemical solution 9 runs out of the substrate 11 at the opposite side of the flat nozzle 13. Thereby, the chemical solution 9 rich in the etchant is supplied onto the film to be etched.

After desired etching has been completed, radiation of the ultraviolet light from the lamp 1 is stopped. The location of the lamp house 2 is stayed as it is, the switching valve 14 is switched to supply ultra-pure water from the flat nozzle 13 into the gap, and to wash away the chemical solution 9 remaining on the substrate 11. At this time, not only the chemical solution 9 remaining on the substrate 11 is washed away, but also the parts that have contacted the chemical solution 9, such as the quartz glass window 3, are simultaneously cleaned.

In the second embodiment, as described above, the supply of the chemical solution 9 from the flat nozzle 13 is performed simultaneously with the radiation of the ultraviolet light from the lamp 1 for wet etching. Therefore the same effect as in the first embodiment is obtained.

Furthermore, in the second embodiment, while ultraviolet light is radiated from the lamp 1 (i.e. during wet etching), the chemical solution 9 is continuously supplied from the flat nozzle 13 into the gap between the quartz glass window 3 and the substrate 11. Thereby, the chemical solution 9 rich in the etchant can always been supplied onto the film to be etched. Therefore, the etching rate can be further increased compared with the first embodiment. Thus, even in the etching reaction wherein the supply of the etchant significantly becomes the rate-limiting factor, there is no need to repeat the supply of the chemical solution and radiation of the ultraviolet light, and the elongation of the processing time and the lowering of the throughput can be prevented. The drying up of the chemical solution 9 due to the evaporation of the chemical solution 9 to change to an irreversible state can also be prevented.

Also in the second embodiment, ultra-pure water is supplied from the flat nozzle 13 by the switching operation of the switching valve 14. Thereby, not only the substrate 11, but also liquid-contacting parts, such as the flat nozzle 13 and the quartz window 3 can be cleaned. Therefore, the installation of the separate nozzle for ultra-pure water is not required, and the etching apparatus can be simplified, and the costs thereof can be reduced.

This invention, when practiced illustratively in the manner described above, provides the following major effects:

According to the present invention, there can be provided an etching apparatus and an etching method having a high etching

selectivity to the base member below the film to be processed, and a high etching rate.

Further, the present invention is not limited to these embodiments, but variations and modifications may be made without departing from the scope of the present invention.

The entire disclosure of Japanese Patent Application No. 2003-21556 filed on January 30, 2003 containing specification, claims, drawings and summary are incorporated herein by reference in its entirety.